Cycloisomerization of Alkynols at Transition Metal Templates

Bernd Weyershausen[a] and Karl Heinz Dötz*[a]

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The metal-assisted cycloisomerization of ω-alkynols to oxacycloalkylidene complexes is reviewed. A variety of low-valent coordinatively unsaturated transition metal templates from group 6 to 10 mediate the cyclization of ω-butynols, -pentynols, and -hexynols to give the corresponding oxacycloalkylidene complexes. In some cases kinetic hydroxyalkylvinylidene complex intermediates can be isolated and characterized.

Introduction

Carbene ligands coordinated to a transition metal center play an important role in both stoichiometric reactions directed towards organic synthesis,[1] and in catalytic processes such as olefin metathesis.[2] Recently, stable nucleophilic carbenes have received a great deal of attention.[3] Their ligand properties resemble those of the well-established phosphane ligands; thus, they may serve as "spectator" ligands in transition metal complexes, which have been successfully applied to olefin metathesis,[4] hydroformylation, and Heck-type reactions.[5] Electrophilic carbenes can be stabilized by coordination to low-valent transition metals; this type of complexes, developed by E. O. Fischer in the 1960s and 1970s,[6] has been increasingly used in stoichiometric C−C bond formation. They undergo ligand-centered reactions which are assisted by a carbonylmetal electron-acceptor fragment; moreover, the metal fragment may serve as a template which activates unsaturated ligands for cycloaddition reactions.[1c,1e,7]

This review deals with the cycloisomerization of alkynols at coordinatively unsaturated transition metal templates of group 6 to 10 metals affording cyclic electrophilic carbene complexes. Although the most versatile route to acyclic Fischer-type carbene complexes is still based on the two-step addition of a nucleophile and an electrophile across the C−O bond in carbonylmetal compounds,[8] the most

[a] Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany
Fax: (internat.) + 49(0)228/735813
E-mail: doetz@uni-bonn.de

Bernd Weyershausen studied chemistry at the University of Bonn. After the diploma thesis with Prof. J. Barluenga at the University of Oviedo (Spain) he started his Ph. D. thesis under the supervision of Prof. K. H. Dötz at the University of Bonn and received his Ph. D. degree there in 1998. Currently, he is working as a postdoctoral fellow in the group of Prof. K. C. Nicolaou at The Scripps Research Institute in La Jolla (USA) supported by a Feodor Lynen Fellowship.

Karl Heinz Dötz was born in 1943 and began his chemical education at the Technical University of Munich where he received his Ph. D. with Professor E. O. Fischer. He then moved towards the borderline between Inorganic and Organic Chemistry, focussed during his habilitation on the organic chemistry of metal carbenes which he applied to novel metal-assisted cycloaddition patterns. In 1986 he became Professor of Organometallic Chemistry at the University of Marburg. In 1992 he was lucky to choose among a few offers, and finally joined the University of Bonn where he was appointed Professor of Organic Chemistry and Co-Director of the Kekulé Institute. He holds visiting appointments in Princeton and Paris, and is a recipient of the Victor Grignard−Georg Wittig Lectureship. His research interests concentrate on organometallic template reactions, stereoselective synthesis, asymmetric catalysis and on carbohydrate chemistry.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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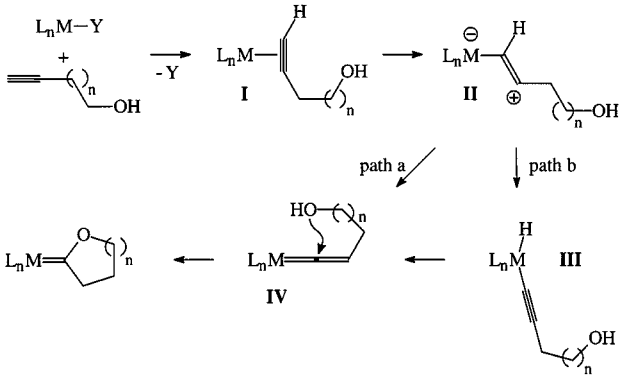
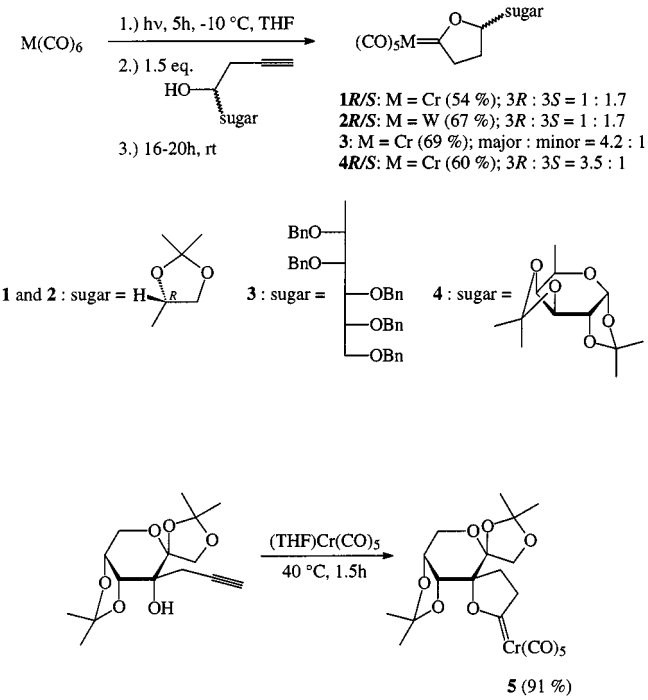
common approach to cyclic Fischer-type carbene complexes is the metal-assisted cyclization of alkynols at low-valent metal templates.[9] Heteroatom-containing cyclic carbene transition metal complexes have also been prepared via ω-haloacyl-,[10] carbamoyl-, alkoxycarbonyl-, or imidometal intermediates,[11] and through the ring opening of epoxides by deprotonated Fischer-type carbene complexes followed by elimination of lithium methoxide upon intramolecular cyclization of the γ-lithium alkoxide substituted complex intermediate.[12] Even direct activation of tetrahydrofuran and other cyclic ethers by $TpIr^{III}$ complexes[13] has been observed with formation of Fischer-type carbene derivatives.[14] Another route is based on the addition of alcohol nucleophiles to vinylidene species accessible from the isomerization of terminal alkynes at a late transition metal center. This strategy, initiated by Chisholm and Clark,[15] has been extended to alkynols which have been treated with a series of group 6 to 10 metals. The formation of the cyclic carbene ligands from ω-alkynols can be rationalized in terms of a vinylidene complex intermediate **IV** which undergoes an intramolecular nucleophilic attack of the hydroxy function at the α-carbon atom of the vinylidene complex (Scheme 1). Experiments using a series of different metal systems have demonstrated that vinylidene complexes can be generated from terminal alkynes by 1,2-hydride migration.[16] These reactions are supposed to involve an initial η^2-alkyne complex **I** which rearranges to its η^1 isomer **II**. The 1,2-hydride shift may occur either directly to the β-carbon atom (path a) or by oxidative addition to a σ-alkynyl(hydrido) species **III** (path b). Whereas calculations favour a direct hydrogen transfer,[17] the oxidative addition pathway is established by experimental evidence.[18]



Scheme 1. Mechanism of the cycloisomerisation of ω-alkynols at metal templates

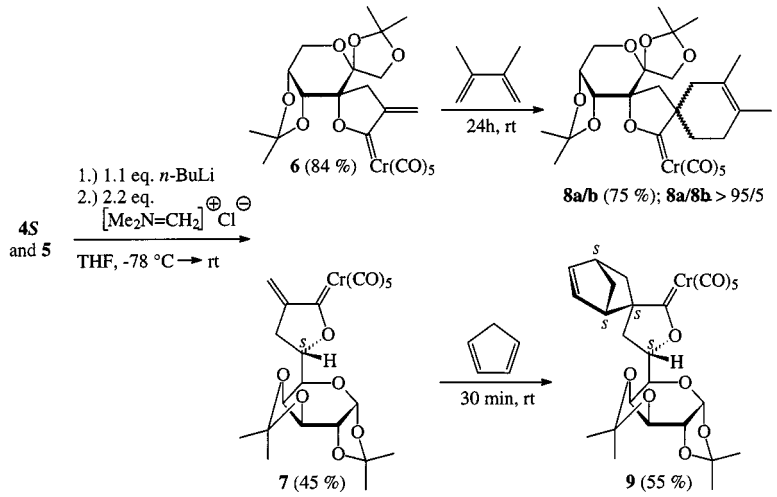
actions.[1c,1e,7] Recently, the authors have started a program aimed at the synthesis of carbohydrate-functionalized oxacycloalkylidene complexes[20] in order to exploit the chiral information provided by the carbohydrate moiety in stereoselective reactions, and to evaluate their potential in the synthesis of natural products and biologically active compounds. As the cycloisomerization of alkynols at coordinatively unsaturated group 6 metals[9] is the most common approach to oxacyclocarbene complexes, interest is focused on the preparation of carbohydrate-derived alkynols and their cyclization at a solvent-stabilized pentacarbonylchromium or -tungsten template. In general, butynols are easily accessible by addition of propargylic organometals to carbonyl compounds.[21] In this case, however, the reagent of choice turned out to be allenylmagnesium bromide[22] which at low temperature undergoes clean γ-addition to the carbonyl functionality of carbohydrate-based aldehydes and ketones to give the desired butynols in yields up to 90%. Carbohydrate-derived aldehydes afford mixtures of diastereomeric butynols, whereas the allenylmagnesium bromide adds with complete diastereoselectivity to carbohydrate-derived ketones. As the diasteromeric butynols are difficult to separate using chromatographic techniques, they were treated as a mixture of diastereomers with pentacarbonyl(tetrahydrofuran)chromium(0) or -tungsten(0) generated by UV irradiation of the corresponding hexacarbonylmetal in tetrahydrofuran at −10°C. The separation of the resulting mixtures of diastereomeric carbene complexes was readily achieved by column chromatography and afforded pure diastereomers of various acyclic[23] and spirocyclic[24] carbohydrate-functionalized 2-oxacyclopentylidene complexes; some examples are shown in Scheme 2.



(Oxacycloalkylidene)chromium, -molybdenum, and -tungsten Complexes

Cyclic Fischer-type metal carbene complexes are valuable tools in organic synthesis.[1] Carbene complexes with group 6 metals are especially synthetically useful reagents, and their synthetic potential is based on both the pronounced α-CH acidity[19] within the alkyl side chain, and on either metal-centered or carbene ligand-centered cycloaddition re-

Scheme 2. Synthesis of carbohydrate-functionalized 2-oxacyclopentylidene complexes



Scheme 3. Diastereoselective Diels–Alder reaction with α-*exo*-methylene-functionalized 2-oxacyclopentylidene complexes

The absolute configuration of the major diastereomers **1*S*** and **2*S*** has been determined by single-crystal X-ray analysis to be (3*S*,4′*R*).[25] In the case of the complex **4** the absolute configuration at C-3 of the minor diastereomer has been determined by single-crystal X-ray analysis of the Diels–Alder product **9** (Scheme 3) to be (3*S*).[26] In general the cycloisomerization of butynols at a tungsten template requires shorter reaction times and gives higher yields of the corresponding carbene complex, indicating that the tungsten template is more reactive than the chromium analogue. Following the procedure reported by Maiorana et al.[27] the carbohydrate-functionalized 2-oxacyclopentylidene complexes could be converted into their α-*exo*-methylene derivatives which serve as potent dienophiles in diastereoselective Diels–Alder reactions (Scheme 3).[20,25,26]

In contrast to the Diels–Alder reaction with 2,3-dimethylbutadiene, the stereoselective addition of cyclopentadiene to the α-*exo*-methylene double bond of complex **7** requires a differentiation not only between *si*- and *re*-side attack, but also between *exo* and *endo* addition. If we take into consideration the absolute stereochemistry at C-3 of complex **7** the diene is expected to add to the α-*exo*-methylene double bond from the top face (*si* side) due to the sterical hindrance of the bottom face (*re* side) caused by the carbohydrate moiety. A single-crystal X-ray analysis of **9** revealed that, due to the steric requirements of the bulky pentacarbonylchromium fragment resulting from the fixed *s-cis* conformation of the (vinylcarbene)metal dienophile **7**, the stereochemical outcome is in accord with an *exo* approach of the diene to the sterically less hindered face (*si* side) of the dienophile (Figure 1).[26][28]

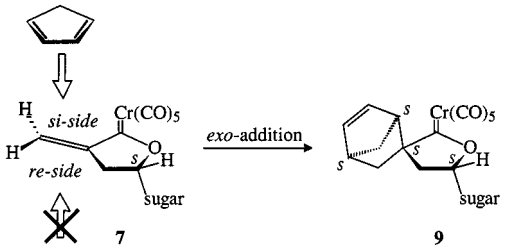
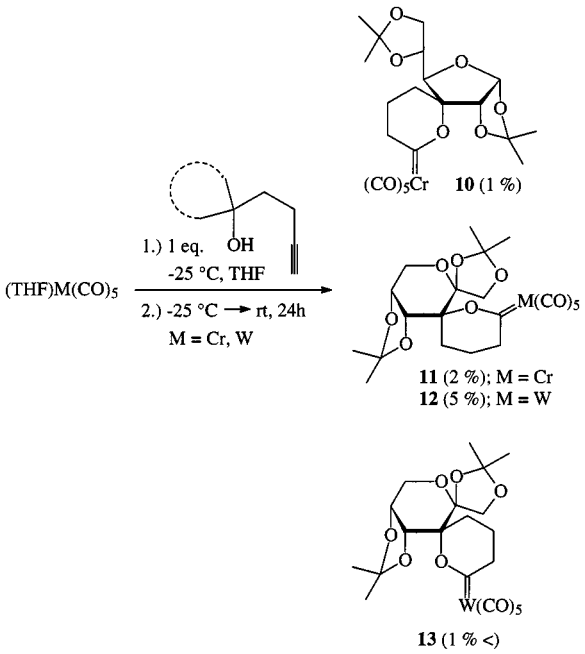


Figure 1. Stereopreference for the addition of the diene to the α-*exo*-methylene double bond

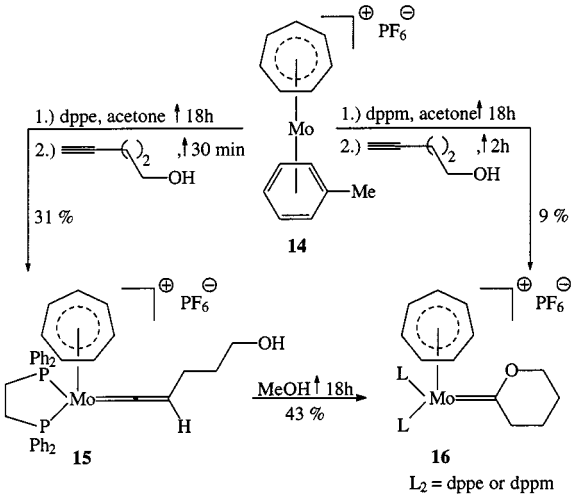
In order to evaluate the potential of this methodology for the synthesis of spirocyclic carbohydrate-derived 2-oxacyclohexylidene complexes the metal-assisted cycloisomerization of suitable carbohydrate-based ω-pentynol precursors was addressed.[29] (Scheme 4). Although in general the cycloisomerization of ω-pentynols gives lower yields compared with the cyclization of ω-butynols, the yields obtained for complexes **10**–**13** were below expectations. This



Scheme 4. Carbohydrate-derived spirocyclic 2-oxacyclohexylidene complexes

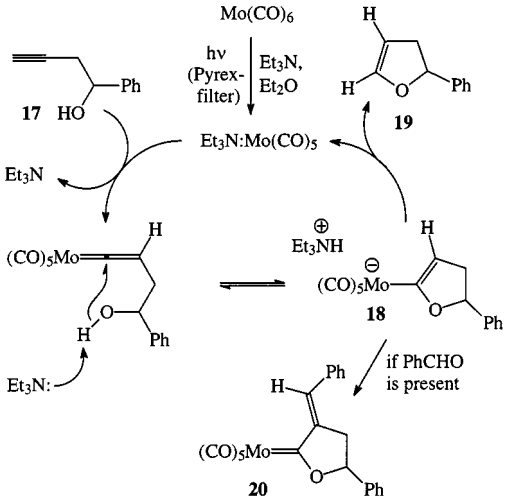
outcome might be rationalized in terms of a slower intramolecular nucleophilic attack of the ω-pentynol hydroxy group at the α-carbon atom of the vinylidene complex inter-

mediate, as a result of a higher flexibility of the hydroxyalkyl substituent combined with a lower thermal stability of the vinylidene complex intermediate. It is noteworthy that in contrast to the reaction of the psicose-based butynol with pentacarbonyl(tetrahydrofuran)chromium(0) affording the complex **5**, the analogous reaction with the psicose-based pentynol resulted in neither isolation of the desired 2-oxacyclohexylidene complex nor in its in situ identification by IR spectroscopy. The more reactive tungsten template allowed the formation of the psicose-derived spirocyclic oxacycloalkylidene complex **13**, as monitored spectroscopically by IR as a decrease in the intensity of the $A_1{}^1$ band of pentacarbonyl(tetrahydrofuran)tungsten(0) at 2074 cm^{-1} along with an increased intensity of the $A_1{}^1$ band of 2-oxacyclohexylidene complex **13** at 2068 cm^{-1}; after 24 h, a small amount of **13** was isolated by column chromatography. Attempts to heat the reaction mixture up to 40°C did not improve the yield, but resulted in decomposition of the solvent-stabilized tungsten template without formation of **13**. So far, there are only a few examples of 2-oxacyclohexylidene group 6 metal complexes which have been prepared by cycloisomerization of the corresponding pentynol.[30][31] The successful isolation and characterization of the hydroxyalkylvinylidene complex **15** suggest that the length and the flexibility of the alkyl chain of the vinylidene complex intermediate as well as the ligands[32] coordinated to the metal template play an important role in the subsequent cyclization[29] (Scheme 5).



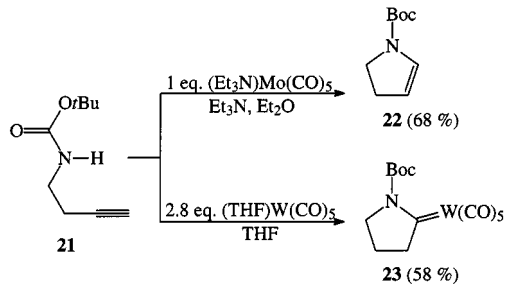
Scheme 5. Isolation and subsequent cyclization of the hydroxyvinylidene intermediate **14**

It has been previously suggested that the formation of oxacycloalkylidene complexes from ω-alkynols proceeds by intramolecular cyclization of a hydroxyalkylvinylidene intermediates.[9b,24c,33] The molybdenum sandwich **14** is able to cycloisomerize ω-pentynol in the presence of DPPM to give the oxacyclohexylidene complex **16** in poor yield.[34] If DPPM is replaced by DPPE the hydroxyalkylvinylidene complex **15** was isolated, which could be converted into **16** in refluxing methanol for 18 h. McDonald et al. reported on a modestly catalytic cycloisomerization of ω-butynols[35] to 2,3-dihydrofurans, and of epoxyalkynes[36] to furans. The pentacarbonylmolybdenum template required for these transformations is best generated by photolysis of hexacarbonylmolybdenum in a mixture of diethyl ether and triethylamine. The mechanism proposed for the cycloisomerization of alkynol **17** to 2,3-dihydrofuran **19** (89% optimized yield using 26 mol-% hexacarbonylmolybdenum) is shown in Scheme 6.



Scheme 6. Proposed mechanism for the catalytic alkynol cycloisomerization

The role of the carbenemolybdenum anion **18** as an intermediate in the catalytic cycle was supported by isolation of the apparent aldol condensation−dehydration[12b,37] product **20**, obtained from the reaction of **17** with $(Et_3N)Mo(CO)_5$ in the presence of benzaldehyde. The metal-promoted cycloisomerization methodology has also been extended to *N*-protected alkynylamines and 2-alkynylanilines.[38] For example, the reaction of *N*-BOC-aminobutyne **21** with 1 equiv. of $(Et_3N)Mo(CO)_5$ in a mixture of triethylamine and diethyl ether as solvent afforded a yield of 68% of 2,3-dihydropyrrole **22**; similarly, azacycloalkylidene complex **23** was formed in a yield of 58% upon the reaction of **21** with 2.8 equiv. of pentacarbonyl(tetrahydrofuran)tungsten(0) (Scheme 7).

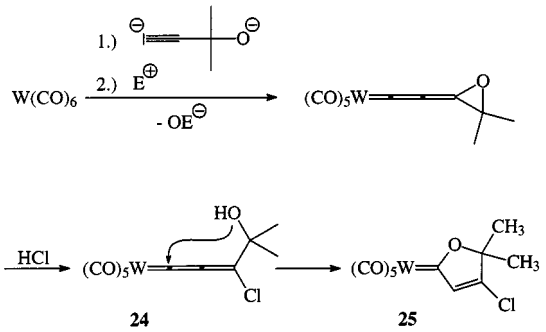


Scheme 7. Cycloisomerization of alkynylamide **21**

This route provides a complementary access to azacycloalkylidene complexes. Their synthesis, so far, has been reported from γ-lactams requiring $K_2[M(CO)_5]$ as a troublesome organometal nucleophile,[39] or from 2-oxacyclopentylidene complexes by aminolysis to give an open-

chain (γ-hydroxyalkyl)aminocarbene complex, which may subsequently undergo nucleophilic cyclization under Mitsunobu conditions[40] to afford 2-azacyclopentylidene complexes.[23][41] The pentacarbonylmolybdenum-catalyzed cycloisomerization is also compatible with alkynyl-substituted carbon nucleophiles such as diethyl 2-(3-butyn-1-yl)-malonate, giving the corresponding cyclopentene derivatives.[42]

Whereas great attention has been paid to 2-oxacycloalkylidene complexes bearing a saturated carbon skeleton, less effort has focused on their endocyclic α,β-unsaturated analogues. The first example of this type of compound was prepared by Berke et al.[43] who studied the reaction of 1,1-dimethylpropynolate with hexacarbonyltungsten. Deoxygenation and subsequent hydrochlorination of the acyltungstate have been suggested in order to generate a hydroxyallenylidene intermediate **24**, which undergoes cyclization to give the 2-oxacyclopentenylidene complex **25** (Scheme 8). Subsequently, complementary routes to endocyclic α,β-unsaturated oxacycloalkylidene complexes have been reported,[37b,44] including classic elimination reactions[12d] or addition of alkyl radicals, generated from epoxides and $(Cp_2TiCl)_2$, to alkynylalkoxycarbene complexes.[31a]



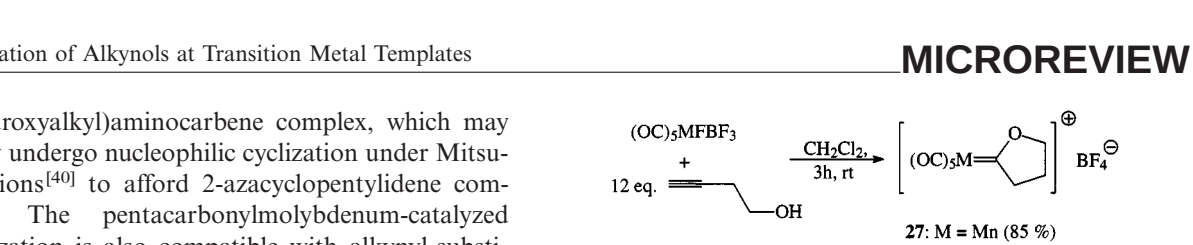
Scheme 8. Synthesis of 2-oxacyclopentenylidene complex **25**

The alkynol cycloisomerization at group 6 metal templates has been successfully applied to the synthesis of natural products and bioactive compounds[30c,30e,45] such as stavudin (d4T)[46] or (±)-andirolactone.[47]

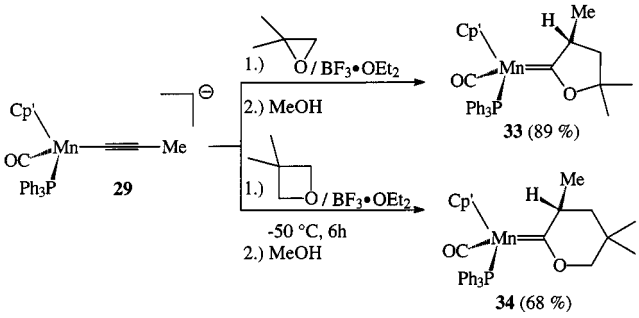
(Oxacycloalkylidene)manganese and -rhenium Complexes

Based on the isoelectronic relation of pentacarbonyl compounds of group 6 and cationic pentacarbonyl compounds of group 7 metal templates, Beck and co-workers[48] extended the alkynol cycloisomerization to cations $[(OC)_5M]^+$ (M = Mn, Re) stabilized by the weakly coordinating tetrafluoroborate ligand. $(OC)_5MFBF_3$ complexes (M = Mn, Re) react with excess 3-butyn-1-ol in dichloromethane to give excellent yields of the cationic 2-oxacyclopentylidene complexes **27** and **28** (Scheme 9).

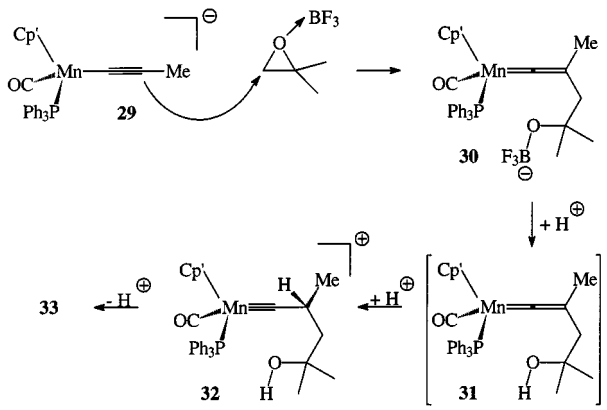
Chiral oxacycloalkylidene complexes can be obtained by ring expansion of oxiranes and oxetanes by the highly nucleophilic anionic alkynyl complex $[(\eta^5\text{-}C_5H_4Me)(OC)(Ph_3P)MnC{\equiv}CMe]^-$ (**29**).[49] Activation of the strained 2,2-dimethyloxirane and 3,3-dimethyloxetane by boron trifluoride–diethyl ether allows for the addition of the organometallic alkynyl nucleophile to afford, after protonation with methanol, the chiral (oxacycloalkylidene)-manganese complexes **33** and **34** in good to very good yields (Scheme 10). The NMR data of the oxycylopentylidene complex **33** indicated the formation of a single pair (*RR*/*SS* or *RS*/*SR*) of diastereomers, implying that the configuration at the metal center efficiently controls the configuration at the chiral ring-carbon atom of the cyclic carbene ligand. Single-crystal X-ray analysis established an (*RS*/*SR*) configuration, placing the methyl substituent and the bulky triphenylphosphane ligand on opposite sides of the (oxacyclopentylidene)metal fragment, as anticipated on the basis of steric arguments. The mechanism proposed for the formation of **33** is shown in Scheme 11.



Scheme 9. Cationic 2-oxacyclopentylidene complexes of manganese and rhenium



Scheme 10. Synthesis of the chiral (oxacycloalkylidene)manganese complexes



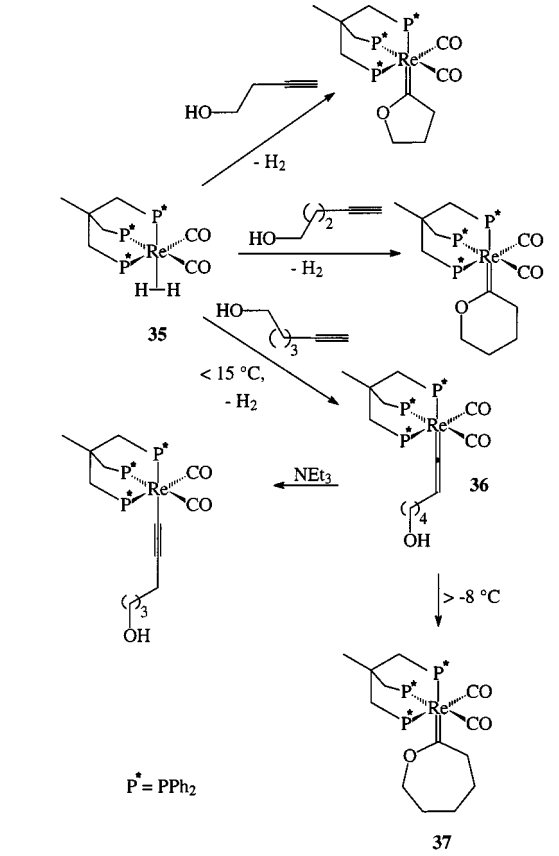
Scheme 11. Proposed mechanism for the formation of **33**

The first step likely involves a Lewis acid assisted ring opening of the epoxide by the nucleophilic attack of **29** to form the anionic vinylidene complex **30**, which represents

another variety of hydroxyalkylvinylidene intermediates, as previously proposed for the cycloisomerization of alkynols at coordinatively unsaturated metal templates. The complex **30** eluded isolation, but its formation was supported by monitoring the reaction by IR; after 10 min, IR absorption bands appeared in the regions characteristic of similar vinylidene complexes prepared by Geoffroy and co-workers[49] [$\tilde{\nu}_{CO}$ = 1886 cm^{-1}, $\tilde{\nu}_{C=C}$ = 1636 cm^{-1}]. Based on the observation of a carbonyl IR absorption band at 1998 cm^{-1}, indicative of a carbynemanganese cation[49][50] and detected in solution after the addition of methanol, the authors favour a stepwise double protonation of **30**, at the oxygen and the β-carbon atoms to form the cationic carbyne complex **32**, over a direct cyclization of the hydroxyalkylvinylidene intermediate **31**. Finally, the hydroxy group is supposed to add to the carbyne carbon atom with concomitant deprotonation to give **33**. It should be noted that the formation of oxacyclopentylidene complex **33** also occurs slowly and with lower yield in the absence of the Lewis acid, whereas for the ring expansion of 3,3-dimethyloxetane the presence of $F_3B \cdot OEt_2$ is crucial.

The mechanism of the oxacycloalkylidene formation was addressed in a very recent comparative study on the reaction of a comparable rhenium template $[\{MeC(CH_2PPh_2)_3\}Re(CO)_2]^+$[51] with a series of ω-alkynols bearing different numbers of CH_2 spacers between the alkynyl and hydroxy functionalities. Previous experiments revealed that the intramolecular addition of the hydroxy group to the α-carbon atom of the hydroxyalkylvinylidene complex is disfavoured with increasing length of the alkyl chain separating the alkynyl and hydroxy moieties.[29,32,49] Consequently, the activation of 5-hexyn-1-ol at a coordinatively unsaturated metal template results in the formation of stable hydroxybutylvinylidene complexes[52] rather than that of the corresponding 2-oxacycloheptylidene isomer. For instance, Bianchini and co-workers succeeded in the interception and charactization of the kinetic (hydroxybutylvinylidene)rhenium intermediate **36**, which they could further convert into the thermodynamically more stable 2-oxacycloheptylidene complex **37** (Scheme 12).[51]

NMR monitoring of the reaction of the dihydrogen complex **35** with a series of ω-alkynols in the temperature range from −50°C to 20°C established the vinylidenerhenium complex **36** as an intermediate in the cycloisomerization of 5-hexyn-1-ol to the thermodynamically stable 2-oxacycloheptylidene complex **37**. In contrast, no homologous intermediate could be detected in the reactions with ω-butynol and ω-pentynol. The hydroxybutylvinylidene complex **36** is stable in solution below −10°C, which allows its unambiguous characterization in solution and its isolation in the solid state. However, it is slowly converted into the 2-oxacycloheptylidene isomer **37** at increasing temperature, and the conversion is fast at room temp. Fischer-type carbene complexes bearing a 2-oxacycloheptylidene ligand are extremely rare compounds. To the best of the authors knowledge, only one other example of the activation of ω-hexynol at a transition metal template, leading to the 2-oxacycloheptylidene complex **38** (Figure 2), has been mentioned in the literature as a footnote without further details.[53] Two other examples of 2-oxacycloheptylidene complexes have been described. The dinuclear dimanganese complex **39** was prepared by reaction of the pentacarbonylmetalate $K[Mn(CO)_5]$ with α,ω-bistriflatopentane,[54] whilst the γ,δ-unsaturated (2-oxacycloheptylidene)chromium complex **40** was synthesized by ring-closure metathesis of the [allyloxy(butenyl)carbene]metal precursor (Figure 2).[55]



Scheme 12. Reaction of $[(triphos)Re(CO)_2]^+$ template with ω-alkynols

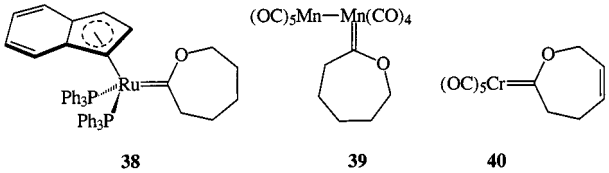
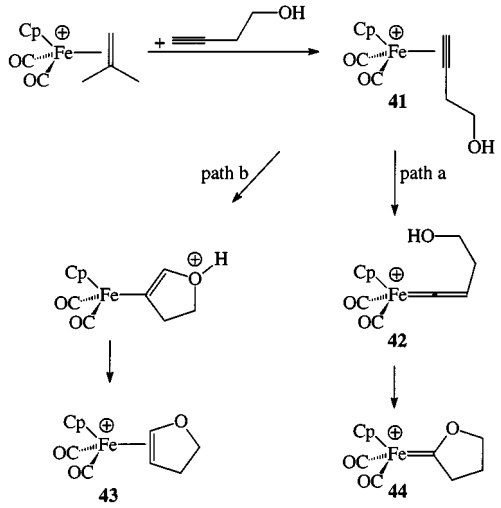


Figure 2. Oxacyclohept(en)ylidene complexes

(Oxacycloalkylidene)iron, -ruthenium, and -osmium Complexes

The reaction of 3-butyn-1-ol with the dicarbonyl(η^5-cyclopentadienyl)iron cation led to a 1:1 mixture of two compounds which, after careful separation by fractional crystallization, were identified as η^2-2,3-dihydrofuran complex **43** and 2-oxacyclopentylidene complex **44** (Scheme

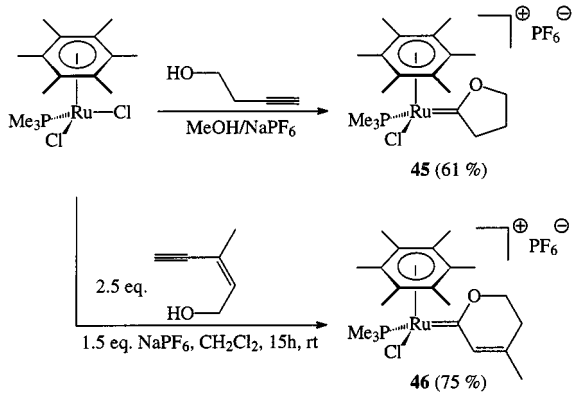
13).[56] Interestingly, the anticipated η^2-alkyne complex intermediate **41** does not only rearrange to the vinylidene complex **42** (path a) as expected, but is also able to undergo direct nucleophilic attack of the hydroxy function at C-4 of the coordinated 3-butyn-1-ol (path b) leading to an η^1-2,3-dihydrofuran-4-yl complex intermediate, which finally undergoes a σ,π rearrangement to give **43**. A chiral metal analogue of **44**, the carbonyl(η^5-cyclopentadienyl)(2-oxacyclopentylidene)(triphenylphosphane)iron(II) cation, was applied to the stereoselective synthesis of 2,2-dialkylbutyrolactones.[57]



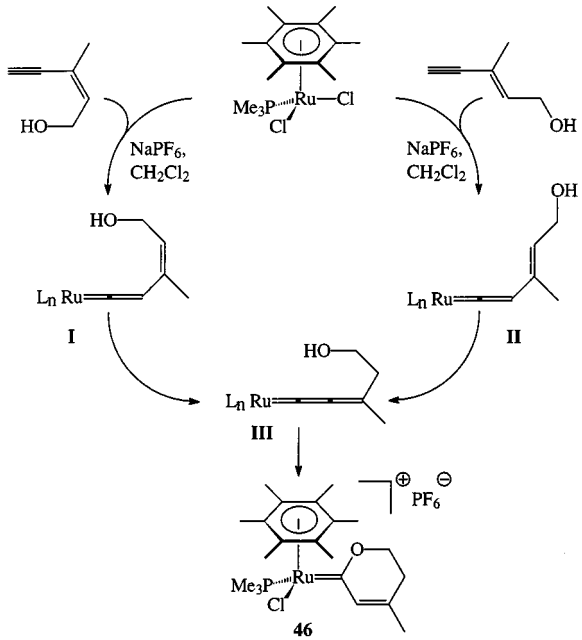
Scheme 13. Competitive pathways for the reaction of 3-butyn-1-ol with $[Cp(OC)_2Fe]^+$

Chiral (oxacycloalkylidene)ruthenium complexes such as **45** are accessible from hexamethylbenzene(trimethylphosphane)ruthenium(II) dichloride and 3-butyn-1-ol (Scheme 14).[58] An extension of the cycloisomerization strategy from simple ω-alkynols to enynols resulted in the synthesis of α,β-unsaturated 2-oxacyclohexylidene complexes,[59] e.g. **46** (Scheme 14).[60] Remarkably, both the (*Z*)- and (*E*)-enynol isomer are activated by the ruthenium template to afford the same α,β-unsaturated 2-oxacyclohexenylidene complex **46**. Obviously, the cycloisomerization does not result from an intramolecular nucleophilic attack of the hydroxy group at the α-carbon atom of vinylidene complex **II** (Scheme 15). Previous results[61] rather suggest the subsequent formation of an allenylidene intermediate **III**[62] involving a 1,3-H migration from the β-carbon atom of **II** to C-4. Thus, the stereochemical information present in the enynol precursor is lost, and the activation of both (*Z*) and (*E*) isomers is expected to lead to the same allenylidene intermediate **III** which, upon intramolecular addition of the hydroxy group to the α-carbon atom, finally produces the α,β-unsaturated cyclic carbene complex **46**. Other (2-oxacyclopentylidene)ruthenium(II) complexes have also been described in the literature.[63]

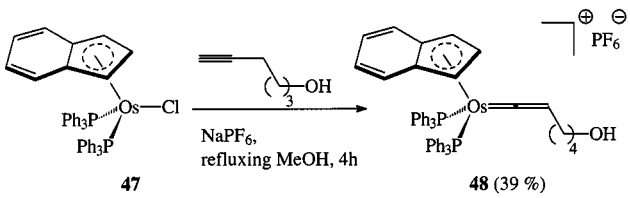
The electron-rich osmium template, provided by (η^5-indenyl)bis(triphenylphosphane)osmium(II) chloride (**47**), also effects the activation of ω-alkynols to metal-coordinated vinylidene compounds.[52b] Whereas ω-butynol and ω-pentynol undergo in situ cycloisomerization to give cycloalkylidene complexes,[64] the activation of ω-hexynol stops at the hydroxybutylvinylidene complex stage **48** (Scheme 16). The stability of **48** reflects the typical increased stability of osmium derivatives compared with their ruthenium analogues,[52b] as demonstrated for the cycloisomerization of ω-hexynol with the ruthenium analogue of **47**.



Scheme 14. (Oxacycloalkylidene)ruthenium complexes **45** and **46**



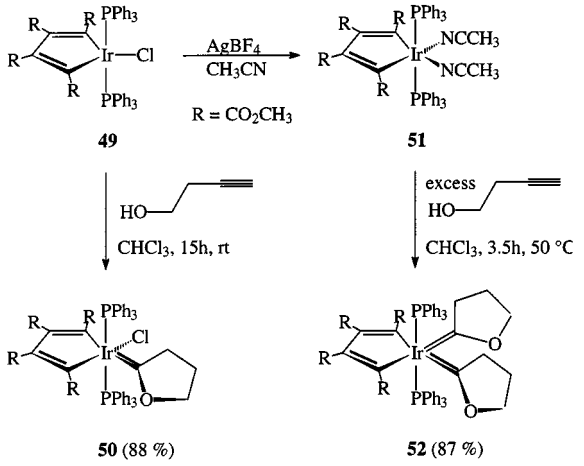
Scheme 15. Proposed mechanism for the formation of **46** from both (*Z*)- and (*E*)-enynol



Scheme 16. Synthesis of (hydroxybutylvinylidene)osmium complex **48**

Oxacycloalkylidene Complexes of Group 9 and 10 Metals

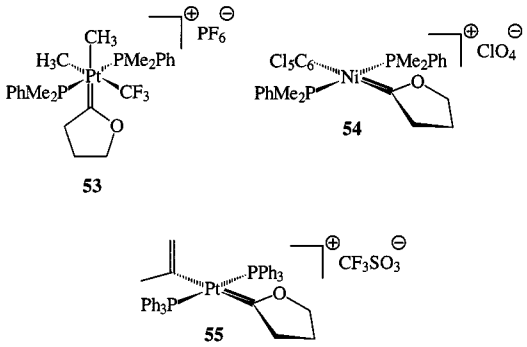
Octahedral (oxacycloalkylidene)iridium(III) complexes were among the first examples of alkynol cycloisomerization products.[65] More recently, the excellent leaving-group properties of triflate ligands have been exploited in the synthesis of square planar (2-oxacyclopentylidene)rhodium and -iridium(II) complexes.[66] The cycloisomerization of alkynols is compatible with the presence of additional metal−carbon σ-bonds. Activation of 3-butyn-1-ol at room temperature by the iridacycle **49** afforded the oxacyclopentylidene complex **50** which represents the first isolable example of a metallacyclic carbene complex (Scheme 17).[67] The metallacyclic template **51**, bearing two labile leaving group type ligands, undergoes a high-yield double cycloisomerization to give the bis(oxacyclopentylidene) complex **52**, which is remarkably stable towards carbene dimerization.[68] The crucial role of the metal template is evident from the comparison of the iridacyclopentadiene **49** with a similar rhodium analogue. The rhodacyclopentadiene did not induce the cycloisomerization of 3-butyn-1-ol; instead, alkyne insertion into the metallacyclic rhodium−carbon bond occurred, followed by reductive elimination to give an aromatic six-membered ring.[67b,69]



Scheme 17. Metallacycle−carbene and −bis(carbene) complexes

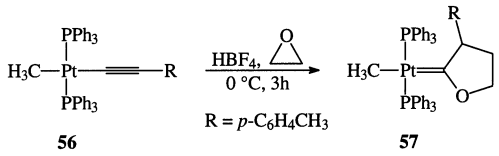
The cationic platinum(IV) complex **53**[15c] was the first example of a carbene ligand coordinated to a metal center in an oxidation state higher than two. Other (oxacycloalkylidene)nickel[70] and -platinum[65][71] complexes, such as **54** and **55**, bearing a metal(II) center have been synthesized by cycloisomerization of 3-butyn-1-ol (Scheme 18).

A complementary route to (2-oxacyclopentylidene)platinum complexes is based on the ring opening of oxiranes by alkynylplatinum(II) complexes assisted by HBF_4 (Scheme 19).[72] Two possible mechanisms, both of which so far lack experimental support, have been suggested for this reaction: The first involves protonation of the alkynyl complex **56**, generating a reactive vinylidene intermediate which may undergo nucleophilic addition of the oxirane oxygen atom at the α-carbon atom. Oxirane opening and subsequent re-



Scheme 18. (Oxacycloalkylidene)nickel and -platinum complexes

cyclization afford the oxacycloalkylidene complex **57**. The second proposal relies on initial protonation of the oxirane followed by β-carbon atom attack of the alkynyl complex **56**, to give a reactive hydroxyethylvinyl intermediate. Final intramolecular cyclization results in the formation of the (oxacycloalklidene)metal complex.



Scheme 19. (Oxacyclopentylidene)platinum complex **57** by ring opening of oxirane

Conclusions

The cycloisomerization of 1,ω-alkynols at transition metal templates provides a general and straightforward approach to oxacycloalkylidene complexes. Recently, this methodology has been successfully extended to alkynylamines and alkynyl-substituted carbon nucleophiles leading to azacycloalkylidene complexes and 2,3-dihydropyrroles, respectively, as well as cyclopentenes. In some cases, hydroxyalkylvinylidene complex intermediates could be intercepted and characterized, supporting the mechanism suggested earlier. In particular, oxacycloalkylidene complexes of group 6 metals have been developed to provide valuable reagents in organic synthesis. The multifunctionality of Fischer-type oxacycloalkylidene complexes may be exploited in subsequent addition reactions of nucleophiles,[23] as well as in metal-[44f,73] or ligand-centered[25,28,44g] cycloaddition reactions aiming at targets both in organometallic and organic chemistry.

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